

REMARKS/ARGUMENTS

A substitute specification is being filed in order to conform with U.S. practice. Headings have been added to the specification. Spelling and grammatical errors have also been corrected. The substitute specification contains no new matter. Amendments have been made to the claims to remove the multiple dependencies and an abstract has been added. An early action on the merits is respectfully requested.

If any additional fees are required in connection with this case, it is respectfully requested that they be charged to Deposit Account No. 02-0184.

Respectfully submitted,

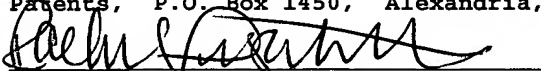
Eva Maria Moser et al.

By 

Gregory P. LaPointe  
Attorney for Applicants  
Reg. No. 28,395  
Tel: (203) 777-6628  
Fax: (203) 865-0297

Date: June 8, 2005

I hereby certify that this correspondence is being deposited with the United States Postal Service as Express Mail in an envelope addressed to: "Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313" on June 8, 2005.

  
Rachel Piscitelli

SUBSTITUTE SPECIFICATION WITH MARKINGS

WO-2004/054728

**Substrate with a polar plasma-polymerised layer**BACKGROUND OF THE INVENTION

[0001] The invention relates to a method for coating substrates with a polar plasma-polymerised layer with a thickness in the nanometer range, having multifunctional properties with long term stability, wherein the process gas contains at least one each of a hydrocarbon compound, which may be substituted, and at least one inorganic gas. The invention also relates to a coated substrate which is produced according to this method and its use.

[0002] It has been known for some time to cover substrates of all types with a thin plasma-polymerised layer. It has been possible to improve the originally poor adhesion of paints, varnishes etc. on the substrate and/or the poor wettability of the substrate with the introduction of low-pressure plasma methods, in particular also with respect to the long term values. The coating of substrates, in particular also of flexible polymer substrates takes place *inter alia* with a view to the surface composition. It is often also necessary to protect the substrate chemically, physically and/or mechanically. If the plasma-polymerised layer has to simultaneously take on a plurality of functions, this is called a multi-functional layer.

[0003] An organic substrate and a method with a coating are known from US 4465738 A, which consists of a lower layer made of a plasma-polymerised alkane, for example methane, and an upper layer made of a plasma-polymerised polar organic component. The coating is distinguished by improved wettability and hydrophilicity.

[0004] WO 99/39842 A1 brought about a breakthrough. Water-free process gases are used to produce a polar coating by means of plasma polymerisation, whereby a previously not attained long term stability can be attained in this use with at least one each of a hydrocarbon compound, which may be substituted, with up to 8 carbon atoms and an organic gas. The plasma coating has an initial surface tension of at least 45 mN/m, which remains unchanged for at least one year. The layer thicknesses are generally below 100 nm, and are therefore in the nanometer range. To carry out the method, according to pages 5 and 6 of WO 99/39842 A1, bridging paragraph, all low-pressure plasma methods are suitable, for example at a pressure of  $1.6 \times 10^{-2}$  mbar. A series of examples is compiled in Table 1 of WO 99/39842 A1. The use of these polar layers with long term stability is extraordinarily diverse as a result of the bonding, i.e. the improved adhesion in relation to polar substances and materials; the printability, scratch protection, anti-fog action and the weldability should be mentioned, in particular.

[0005] ~~The present patent application is based on the object of providing~~ It is an object of the present invention to provide a method for coating substrates of the most varied types with a plasma-polymerised layer and creating a product of the type mentioned at the outset which further improves the properties even with a widened substrate base, in particular increase the adhesion on the plasma-polymerised layer and of this layer on the substrate.

#### SUMMARY OF THE INVENTION

[0006] The object is achieved according to the invention in that coating is carried out - (a) in a first zone or stage with process gases which contain at least one hydrocarbon compound, at least one hydrocarbon compound with nitrogen-containing or

nitrogen- and oxygen-containing functional groups and/or at least one nitrogen-containing or one nitrogen- and oxygen-containing inorganic gas, - and (b) in a second zone or stage with nitrogen-free process gases which contain at least one hydrocarbon compound, at least one hydrocarbon compound with oxygen-containing functional groups and/or at least one oxygen-containing inorganic gas.

~~[0007] Special and developing embodiments of the method are the subject of dependent claims.~~

#### DETAILED DESCRIPTION

[0008] Using efficient gas mixtures which can be used independently of the pressure range and of the type of discharge, plasma-polymerised polar protective layers with long term stability are possible with the method according to the invention. A way of combining a plurality of layers for multifunctional properties is disclosed. In the case of more than two layers, it is important to the invention that the layer deposited directly onto the substrate is nitrogen-containing, but the upper layer is nitrogen-free but oxygen-containing.

[0009] Polar plasma layers, which contain oxygen- and/or nitrogen-containing functional groups, can be produced at much higher pressures than are usual in low pressure methods; because *inter alia* a certain proportion of air does not damage the processes, but may even be useful, a pressure range up to 1,000 mbar is possible. Under these preconditions, practically all known plasma coating technologies for planar or three-dimensional workpieces, can be used.

[0010] The plasma layer according to the invention can be connected downstream or upstream to a production step virtually as desired, regardless of whether the workpiece has already been sluiced in a vacuum chamber and, for example, a metallization is

to take place subsequently or whether a bonding coating taking place at atmospheric pressure prior to printing is involved. The workpiece can also be used directly as an anti-fog functional layer.

[0011] The surface of the plasma-coated workpieces may be smoother than the untreated substrate. Gentler surface contours favour the surface wetting and therefore the anti-fog effect which is important here. The nitrogen-containing process gases of the first zone or stage, on the one hand, bring about good anchoring of the plasma layer on the substrate and, on the other hand, depending on the control of the process parameters (output, gas mixture) can smooth and/or structure or modulate the surface to a greater or lesser degree. The etching action of aggressive gases, such as for example laughing gas, ammonia and oxygen is primarily decisive for this effect, in particular when these gases are added with an increased proportion.

[0012] XPS (X-ray photoelectron spectroscopy) measurements show, or confirm, the expected enrichment with oxygen and nitrogen and the incorporation of oxygen, in particular as hydroxyl, carbonyl or carboxyl (ester) groups.

[0013] The plasma-polymerised layers which are deposited according to the invention are distinguished by their controllable multifunctionality; the plasma layer can be adapted to the respective use by varying parameters. All plasma-polymerised layers which are produced according to the invention have long-term stability in common. A further, generally required property is a permanent high surface tension of the plasma-polymerised polar layers, which are therefore hydrophilic and this also means good bonding with respect to dispersion dyes. Further examples of multifunctionality of the polar layers are the mentioned anti-fog effect, the formation of a scratch protection layer, a barrier layer against additives, gases and

liquids, which, on the one hand, migrate from the substrate onto the surface or may be deposited by the environment on the surface, or a flame protection layer.

[0014] The plasma-polymerised layers are preferably deposited at a process pressure  $p$  between  $10^{-3}$  and 1,000 mbar, in particular between 0.1 and 500 mbar. For the reasons mentioned, the process pressure is significantly higher than in comparable conventional methods, in particular also higher than according to WO 99/39842. The plasma reactor is expediently pumped out in advance to a base pressure which is lower than the process pressure, preferably at least about 10 times lower, then filled with process gas. After a coating process below 1,000 mbar, the plasma reactor is flooded, for example with air, nitrogen or argon until the normal pressure is attained and the reactor can be opened. Flooding with argon is too expensive for most processes and air is generally sufficient for this.

[0015] The organic compound in the process gas may be a pure hydrocarbon compound or a hydrocarbon compound with substituted functional groups, in particular oxygen- and/or nitrogen-containing polar functional groups.

[0016] The hydrocarbon compounds themselves may be of the most varied nature:

[0017] - alkanes, for example methane, ethane, propane

[0018] - alkenes, for example ethylene, propylene

[0019] - alkynes, for example acetylene

[0020] - polyenes, i.e. hydrocarbons with a plurality of double bonds,

[0021] in each case in aliphatic, alicyclic or aromatic form, without or with branch(es).

[0022] Acetylene ( $C_2H_2$ , ethyne) is used in particular as the layer-forming process gas, the other process gases control the

functional groups and can thus also remove atomic layers from the surface.

[0023] The hydrocarbons may, as mentioned, be substituted with halogens, such as chlorine and/or fluorine, or be substituted with functional polar groups. Examples of functional polar groups are hydroxyl, carbonyl, carboxylic acid, carboxyl ester, amine, imine, amide and/or conjugated nitrile groups.

[0024] When adding silicon-containing process gases, additional  $\text{SiO}_x$ -containing functional groups are generated in the lower and/or upper layer and the oxygen content thereby increased. In the process, C-atoms can partly be replaced by Si-atoms.

[0025] Both for substituted and non-substituted hydrocarbon compounds, it is advantageous if the molecules contain up to a maximum of 8 C-atoms.

[0026] The inorganic component of the process gases advantageously comprises oxygen, carbon dioxide, carbon monoxide, nitrogen,  $\text{NO}_x$ , ammonia, hydrogen, at least one halogen and/or at least one noble gas, but is preferably water-free.

[0027] The process gases for depositing the lower and upper layer basically differ only with respect to the nitrogen and/or oxygen content.

[0028] The two-stage coating according to the invention is also indicated in particular for food packagings. It has been shown that nitrogen-containing gases clean the substrate surface with the formation of a CN-bond. This leads in addition to improved anchoring of the functional polar groups, which in turn results in a higher chemical resistance. A nitrogen-free, oxygen-containing upper layer is also deposited on this lower layer, which may also be very thin, for example about 0.3 nm, so the nitrogen-containing layer cannot come into contact with food or other nitrogen-sensitive objects.

[0029] Two plasma sources are preferably used for depositing a lower and an upper layer. In the first zone/plasma source, a nitrogen-oxygen-hydrocarbon-containing gas mixture is supplied, for example, and a lower layer deposited on the substrate. With the second zone/plasma source, an upper layer is deposited on the lower layer from a nitrogen-free, oxygen-hydrocarbon-containing process gas mixture. Plasma chambers with two plasma sources, as are used here, are known to the person skilled in the art.

[0030] According to a further variant, a single plasma source can be used and the nitrogen-hydrocarbon-containing or nitrogen-oxygen-hydrocarbon-containing gas mixture may be introduced first, and the oxygen-hydrocarbon-containing process gas mixture be introduced during the second pass.

[0031] With respect to the product, the object is achieved according to the invention in that a plasma-polymerised polar layer in the nanometer range is applied as a nitrogen-containing lower layer applied to the substrate, and a nitrogen-free, oxygen-containing polar upper layer is applied thereon. Special and developing embodiments of the product emerge from the dependent claims.

[0032] The nitrogen-containing lower layer preferably has a proportion of 40 to 90% of the total layer thickness, the polar upper layer has a proportion of 60 to 10% of the total layer thickness, preferably about 50% in each case. The entire layer thickness is preferably in the range of 1 to 100 nm. The coated substrates can be welded to one another.

[0033] In a layer, with a lower and upper layer made of hydrocarbon compounds with oxygen-containing functional groups, the oxygen/carbon ratio is preferably in the range of 0.03 to 0.8 in each case, and in the lower layer the nitrogen/carbon ratio is in the same range. The polar upper layer, averaged in



the uppermost about 2 nm, i.e. on the surface, preferably has an oxygen/carbon ratio of 0.2 to 0.6, preferably of 0.3 to 0.5 and a permanent surface tension of at least 50 mN/m. Carboxyl groups raising the oxygen content can be formed on the surface of the upper layer. A good anti-fog effect is ensured, in particular, with the high surface tension, in particular with a suitable surface topography.

[0034] The layer according to the invention can be deposited on all types of substrates, for example on polymer, glass-like, ceramic, metallic or natural surfaces, in particular on a polycarbonate, polyethylene terephthalate, polypropylene, polyethylene, polyamide, fluoropolymers, wool, cotton, silk, glass, ceramic or else composite materials, all materials including natural, in the form of films, moulded bodies, containers, textiles, non-wovens, membranes, granules, powders, fibres, grids and yarns, containers and also in the form of coated or activated or treated surfaces of materials of all types.

[0035] A product according to the invention is described in more detail with the aid of a layer construction shown schematically in Fig. 1. This figure shows a coated substrate 10 with a substrate 12, a lower layer 14 and an upper layer 16. The two polar plasma-polymerised layers 14, 16 in the present case have a total thickness  $d$  of about 10 nm. The lower layer 14 is nitrogen-containing, it has excellent adhesion with the substrate 12. A possible amine formation could be disadvantageous because of the lower layer 14. This disadvantage is prevented by the oxygen-containing, but low in nitrogen to nitrogen-free upper layer 16.

**Example: Multilayer deposit with a microwave discharge**

A thin lower layer 14 is deposited on a substrate 12 with a microwave source at 2.45 GHz, using a process gas mixture of acetylene, carbon dioxide, laughing gas and argon, which is introduced in the first zone at the plasma source or at the first plasma source. In the second zone or the second plasma source, the gas mixture acetylene, carbon dioxide and argon is introduced to produce the upper layer. At a pressure range of 0.01 to 320 mbar and an output range of 60 to 2,000 watt, surface tensions of 54 to 75 mN/m were attained on the substrates polyester, polypropylene and polyethylene, and have a polar fraction of 23 to 51 mN/m and are characterised by an oxygen to carbon ratio of 0.3 to 0.5 and a carboxyl groups to carbonyl groups ratio of 0.2 to 1.2. The surface tension can *inter alia* also be controlled by the feed speed. The ratio of oxygen to carbon and the ratio of the carboxyl groups to the carbonyl groups in the uppermost atom layers of the deposited layers was determined with the surface-sensitive XPS (photoelectron spectroscopy).

The same layer properties can be attained with all other discharge types with respective excitation frequencies of zero to 20 GHz and can be attained in each case with or without magnetic field support. Mentioned by way of example are DBDs (dielectric barrier discharges), low pressure to atmospheric pressure glow discharges, APNEDs (atmospheric pressure non-equilibrium discharges), surface discharges, plasma nozzles and plasma wide beam burners.